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Electrochromic Investigation of Manganese Oxide Thin Films by Spray Pyrolysis Technique

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Abstract: ***Thin films of MnO_2 are well suited for Electrochromic Photo-Voltaic (ECPV) effect and superconducting phenomenon (such as solar cells) due to its electrical, optical and electrochromic properties. MnO_2 thin films were prepared on glass substrate using a simple and low-cost chemical spray pyrolysis technique at different substrate temperature. The MnO_2 films were characterized by X-ray diffraction (XRD), transmittance, ultraviolet-visible (UV-VIS) optical spectroscopy and colouration efficiency. The XRD pattern reveals that MnO_2 films possess cubic structure. Transmittance activity of the sample was carried out by optical absorption studies. The indirect band gap of the material increases with increase in temperature. The dynamic of ion exchange was studied with CV, CA and CC. The maximum colouration efficiency observed is 17 cm^2/C.***

Keywords: Colouration efficiency, Electrochromism,Manganese oxide, Spray pyrolysis, XRD

1. Introduction

An electro active species often exhibits new optical absorption bands (i.e. shows a new colour) in a accompaniment with an electron-transfer or redox reaction in which it either gains or losses an electron. Such colouration was first termed as electrochromism.An electrochromic (EC) material is able to change its optical properties in a reversible and persistent way under the action of a voltage pulse. This change is due to the formation of colour centres (or defect complex) or to an electro-chemical reaction that produces a coloured compound. The species that becomes coloured during redox reaction is called electrochrome. After a pulse of current effecting electron transfer at the working electrode has evoked the colouration; the colour persists, thereby producing memory effect. Current in opposite direction reverses the electrochemical process and the display reverts to the colourless or bleached state.

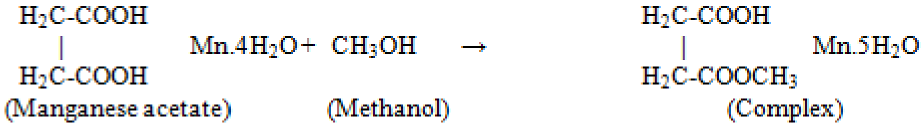
Electrochromism (EC) is exhibited by a number of materials, both inorganic and organic liquid and solid substances. Apart from conductive electrode (metal or conducting glass), electrochromic species can be all liquid (e.g. the ferro-ferricynide system cited), or all solid, as a film or it can undergo liquid to solid conversion following oxidation or reduction where the electrochromic film is solid. The ionic diffusion involved here, or the intrinsic rate of electron uptake or loss, will determine the rate of electrochromic operation. The most widely studied inorganic substance is solid tungsten trioxide WO_3, in which the introduction of small amount of W^v give M_xWO_3(M is cation) again allows intense optical absorption, or with particular values of x in this case of reflection. The change in optical properties makes electrochromic materials of considerable interest for optical devices of several different types such as elements of information display, light shutters, smart windows. Electrochromic optical switching devices known as “smart windows” can be used for variety of applications. One of the most promising applications is for the regulation of incident solar energy and glare in building, vehicles, air-crafts, space-crafts and ships. “Smart windows” technology is a more attractive alternative for substantial energy saving and is in practical use to some extents in many developed countries.

Manganese oxide (MnO_2) is a transition metal oxide. It is black in colour and is used as electrode materials [1, 2], oxidizing agent, electrochemical catalysts [3]. MnO_2 of different structures are deposited using several techniques such as sol-gel [4], thermal evaporation in vacuum [5], MOCVD [6]. Manganese oxide of different structure (MnO, Mn_2O_3, MnO_2 and Mn_3O_4) is usually prepared by varying calcinations condition of starting chemical precursor bulk or film. They can also be prepared each other by varying the temperature and atmosphere (vacuum or air, oxygen, hydrogen etc.,) of the calcinations [6]. Electrochemistry of MnO_x electrodes has been widely studied as originated from their application for active materials in primary batteries, typically preparation of MnO_2 electrode by galvanostatic electrolysis has been performed [7]. Furthermore, MnO_x thin films have received much attention as electrochromic (EC) materials [8, 9]. Several preparation methods of EC MnO_x thin films including galvanostatic electrolysis [10, 11], chemical vapor deposition [12], thermal decomposition [13] and electron beam evaporation [14] have been proposed.MnO_2 is prepared in the form of thin films on glass substrate by chemical spray pyrolysis technique and their structural, optical properties and electrochromic properties are discussed. (Fig.1.1)

2. Experimental Procedure

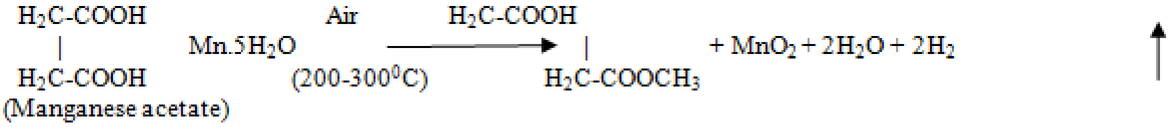
2.1 Film Formation

MnO_2 thin films were grown on glass substrate using a typical spray pyrolysis technique. The spraying solution was prepared by dissolving appropriate quantity of precursor powder (manganese acetate) in methanol at room temperature according to equation,



$$\underset{\text{(Manganese acetate)}}{\begin{matrix}H_2C\text{-}COOH\\ |\\ H_2C\text{-}COOH\end{matrix}}\ Mn.4H_2O + \underset{\text{(Methanol)}}{CH_3OH} \rightarrow \underset{\text{(Complex)}}{\begin{matrix}H_2C\text{-}COOH\\ |\\ H_2C\text{-}COOCH_3\end{matrix}\ Mn.5H_2O}$$

This solution is then atomized by compressed air at the pressure of 1 kg/cm^2 on to the ultrasonically cleaned glass substrates. The sprayed droplets undergo solvent evaporation, solute condensation and thermal decomposition thereby resulting in the formation of manganese oxide thin film. The chemical reaction that takes place is given by equation,



$$\underset{\text{(Manganese acetate)}}{\begin{matrix}H_2C\text{-}COOH\\ |\\ H_2C\text{-}COOH\end{matrix}}\ Mn.5H_2O \xrightarrow[(200\text{-}300^0C)]{Air} \begin{matrix}H_2C\text{-}COOH\\ |\\ H_2C\text{-}COOCH_3\end{matrix} + MnO_2 + 2H_2O + 2H_2 \uparrow$$

The substrate temperature was maintained at 200°C, 250 °C and 300 °C (± 2 °C) through a thermocouple as a sensor for temperature controller. The spray rate was kept constant at 12cc/min. The carrier gas flow rate was kept constant at 15 lit/min.

The MnO_2 films were subjected to X-ray diffraction technique to investigate the structural properties using a X-ray diffractometer (Philips PW1710) with CuKα radiation (λ = 1.5406 Å). Transmittances versus wavelength measurements were made using UV-VIS- NIR spectrophotometer (Hitachi model 330).

2.2 Configuration of Electrochromic Cell

The conventional three electrode cell was used to carry out CV, CA and CE experiment. The configuration of cell was as follows,

$FTO/MnO_2/0.01M\ H_2SO_4/C;\ SCE$

With MnO_2 deposited on FTO as a working electrode, 0.01M H2SO4 as an electrolyte, C: counter electrode (graphite), SCE is saturated calomel reference electrode to which all measured voltages were referred.

3. Results and Discussion

3.1 Structural Analysis

The structural elucidation of MnO_2 film was shown in Fig. 1.2. The structural identification of MnO_2 thin films deposited at various substrate temperatures from manganese acetate was carried out with X-ray diffraction. (The diffraction pattern obtained for samples T1, T2, T3 are as shown in Fig. 1.2.) The observed XRD patterns were compared with the JCPDS data [15]. The observed'd' values agree well with the standard'd' values and it was observed that all samples exhibit peaks corresponding to (104), (001), (311), (400) planes. The comparison with JCPDS data confirms the formation of $Mn(OH)_2$ and MnO_2. The standard and observed'd' values with corresponding (hkl) planes are listed in Table 1.

The samples T1 prepared at lower temperature 200°C consists of $Mn(OH)_2$ phase indicating an incomplete thermal decomposition of manganese acetate. It was also observed that prominence of MnO_2 phase was found to improve with increase in deposition temperature. The films prepared at 250°C consist of $Mn(OH)_2$ & λ- MnO_2 and the films prepared at 300°C consist of λ- MnO_2 films.

3.2 Transmittance Analysis

The films were further analyzed by optical absorption studies as well as transmittance study. The variation of optical absorption density 'αt' with the wavelength 'λ' for the films were carried in the wavelength range 400 to 800 nm with UV spectrometer. This optical data were further analyzed to calculate the band gap energy of MnO_2 samples using the relation,

$\alpha = \alpha_o (h\nu - E_g)^{\mathbf{n}}$

Where α_o-constant, hν-photon energy, E_g - band gap energy

n= 1/2 for direct allowed transition
n = 2 for indirect allowed transition

Fig.1.3 shows the variation of $(\alpha h\nu)^2$ Vs (hν) for all samples and fig.1.4 shows the variation of $(\alpha h\nu)^{1/2}$ Vs (hν). The extrapolation of the straight line portions of the plots $(\alpha h\nu)^2$ Vs (hν) to zero absorption coefficient gives the values of direct band gap energy and extrapolation of the plots $(\alpha h\nu)^{1/2}$ Vs (hν) to gives the values of indirect band gap energy. It is found that indirect band gap of the samples increases with increase in temperature. The direct band gap energy for the samples at 250°C is minimum as compared to other samples.

3.3 Electrochromical Analysis

3.3.1 Cyclic Voltammetry (CV)

The voltammograms recorded at various scan rates (10 to 100 mVS^{-1}) for sample T1 and T2 are shown in 1.5 and fig. 1.6 resp. All the values of i_{pc}, i_{pa}, E_{pc} and E_{pa} obtained from the recorded voltammograms are listed in Table 2.The sample T2 shows higher cathodic and anodic peak currents than the sample T1, which indicates that the number of H^+ ions intercalated and de-intercalated in T2 is more than T1. Result shows that the area under the curve decreases as scan rate increases and the area under the curve for T1 sample is always greater than T2 for various scan rates

3.3.2 Chronoamperometry (CA)

Fig.1.7 shows variations of current versus time transients for MnO_2 thin films in 0.01M H_2SO_4 electrolyte at voltages ± 0.4 V, ± 0.6 V, ± 0.8 V, ± 1 V. The colouration time and bleaching time estimated from fig. 1.7 and are listed in Table 3. It has been seen that the coloration as well as bleaching time increases with potential step. The maximum colouration time and bleaching time are 12.52 Sec and 32.07 Sec. resp. The reversibility of the reaction is 0.528 shows that the reaction is quasi-reversible.

3.3.3 Optical Studies

For the coloured state, the transmittance at 34% and for bleached state is about 46%. The change in transmittance is caused by an increase in the concentration of conduction band electrons. The free conduction band electron increases the absorption known as Drude absorption, so that the film become coloured. For the bleached state, the electrons occupied the levels in conduction band giving rise to an apparent increase in the band gap.

3.3.4 Colouration Efficiency

It is seen that colouration efficiency increases in potential step. It is noted that amongst these potential steps, sample exhibits maximum colouration efficiency of about 17 cm^2/C at potential step ± 0.76 V, which is the result of largest optical modulation at 630 nm wavelength for smaller charge intercalation. (Wavelength of 630 nm is the most sensitive to human eye, therefore CE is calculated at 630 nm). The reported CE value is about $7cm^2/C$, for MnO_2 films made by electrodeposition.

3.3.5 Diffusion Coefficient

Diffusion coefficient measures the depth of intercalation of ions. The diffusion coefficient is given by,

$$D^{1/2} = i_p / 2.6886 * 10^5 * n^{3/2} * conc. * v^{1/2} * A$$

Where i_p is cathodic peak current, ν is scan rate, A is area of film.

In case of MnO_2, the diffusion coefficient increases with increase in scan rate. It is observed that the diffusion coefficient is larger for T2 than T1 for various scan rates. The maximum value of diffusion coefficient for T1 and T2 are 4.925 x 10^{-9} cm^2/sec and 7.22 x 10^{-9} cm^2/sec resp. The value of ‘D’ depends on charge passed and hence extent of electrode reaction. The maximum value of insertion coefficient (X) is 0.0059. The insertion coefficient is given by,

$$X = Q_i M / F \rho A t$$

Where Q_i is charge intercalated, M is the molecular weight, F is Faraday’s constant, A is area, ρ is the density of bulk material and t is thickness.

The value of X decreases with increase in scan rate.

4. Conclusions

MnO_2 thin films were prepared using by spray pyrolysis technique. The structural analysis revealed the cubical nature of the film; it is also observed that the prominence of MnO_2 phase was found to improve with an increase in deposition temperature.

The indirect band gap energy of the material increases with increase in temperature. The dynamic of ion exchange was studied with CV, CA, and CC. The sample T2 exhibits maximum EC colouration efficiency and is 17 cm^2/C. The maximum transmittance is observed for sample T2.

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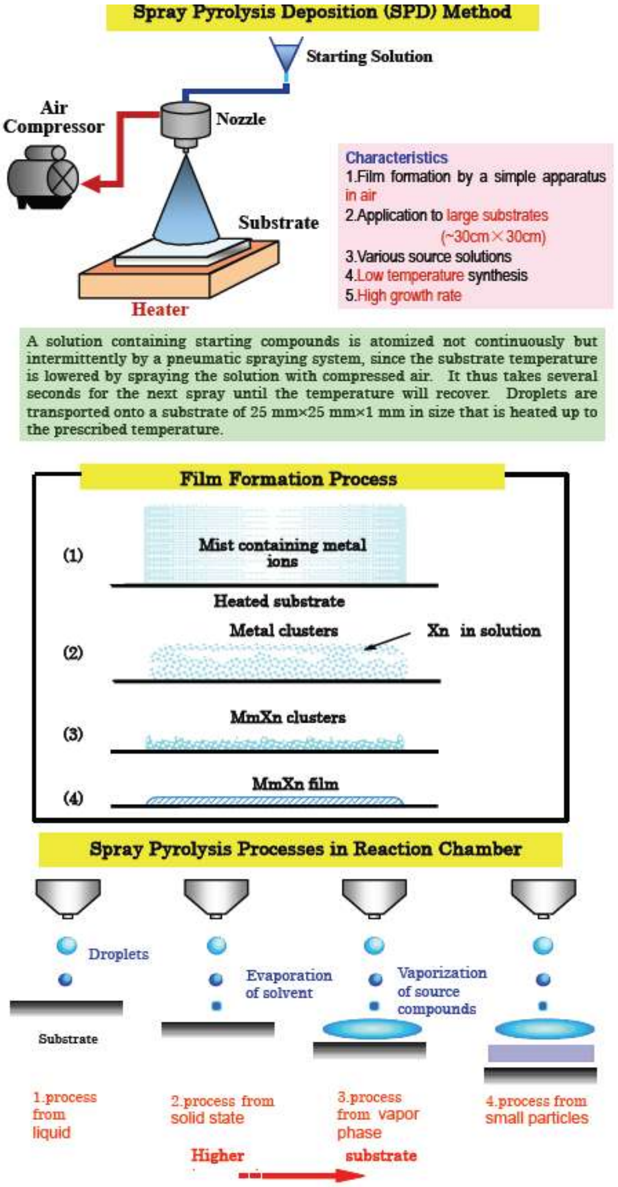
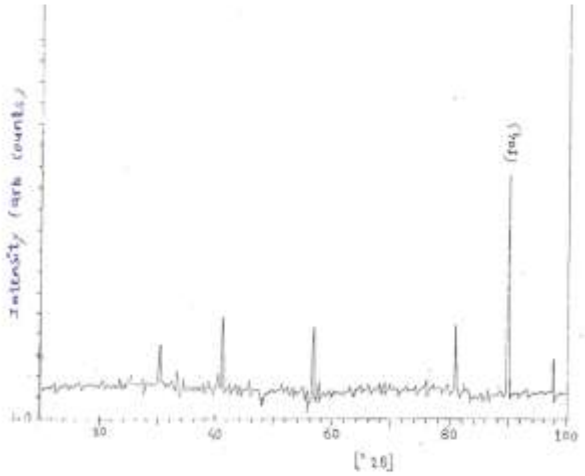


Characteristics
1.Film formation by a simple apparatus in air
2.Application to large substrates (~30cm×30cm)
3.Various source solutions
4.Low temperature synthesis
5.High growth rate

A solution containing starting compounds is atomized not continuously but intermittently by a pneumatic spraying system, since the substrate temperature is lowered by spraying the solution with compressed air. It thus takes several seconds for the next spray until the temperature will recover. Droplets are transported onto a substrate of 25 mm×25 mm×1 mm in size that is heated up to the prescribed temperature.

Figure 1.1: Spray pyrolysis technique



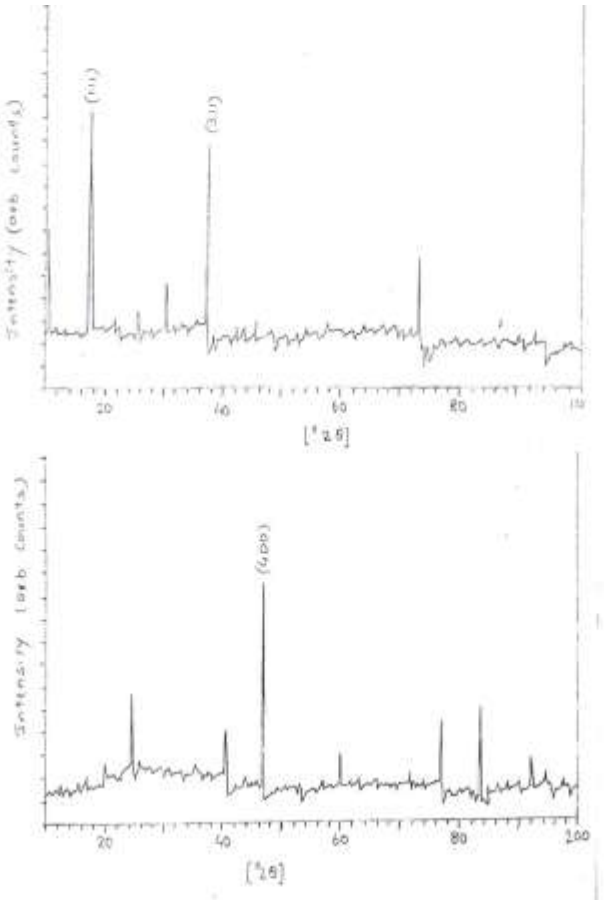


Figure 1.2: The diffraction pattern obtained for samples T1, T2, and T3

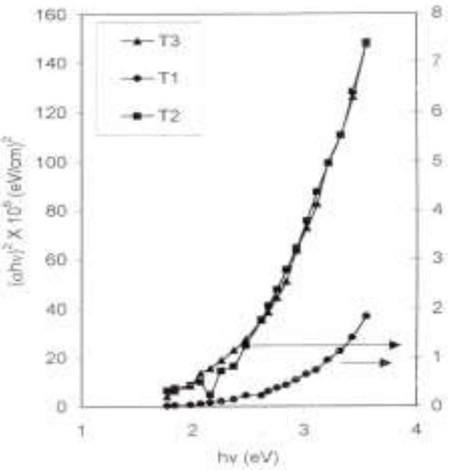


Figure 1.3: Direct band gap energy

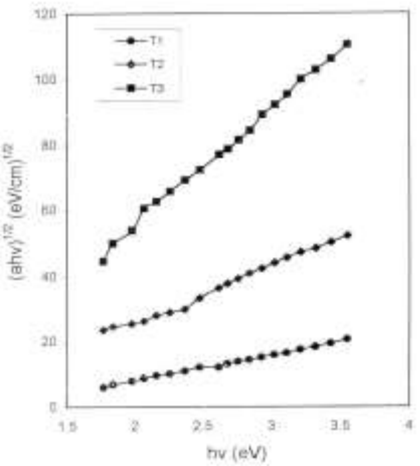


Figure 1.4: Indirect band gap energy

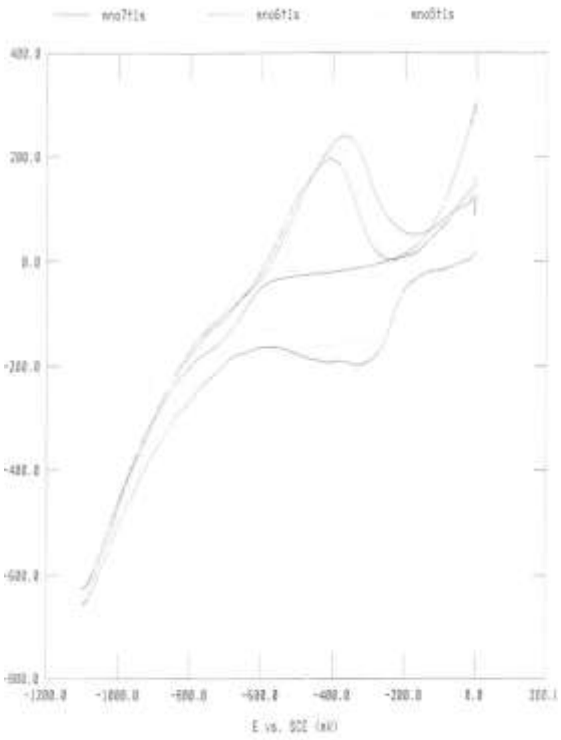


Figure 1.5: Cyclic Voltammogram of T1

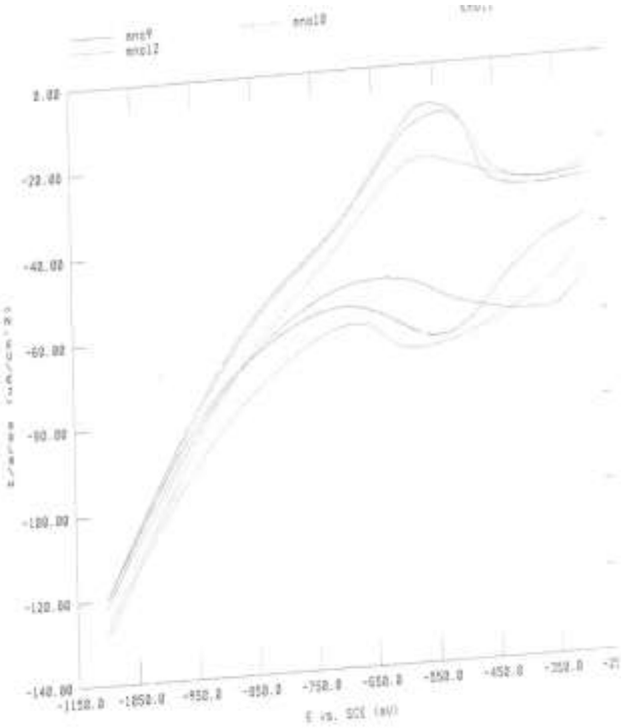


Figure 1.6: Cyclic Voltammogram of T2

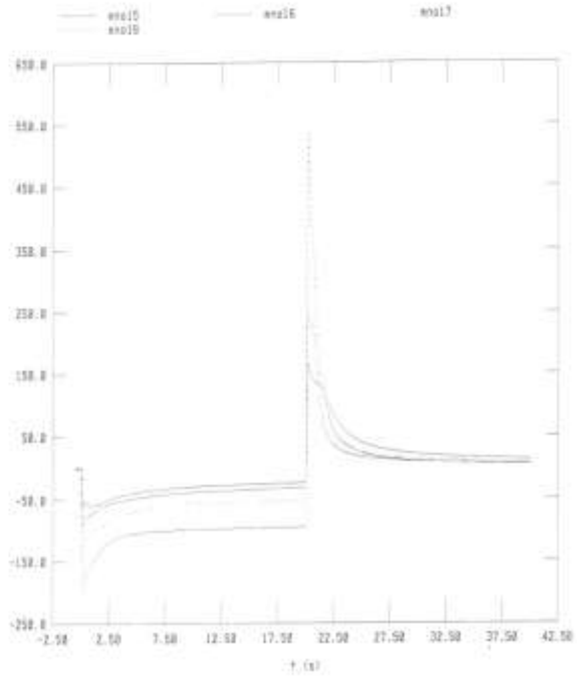


Figure 1.7: Chronoamperometry of T2

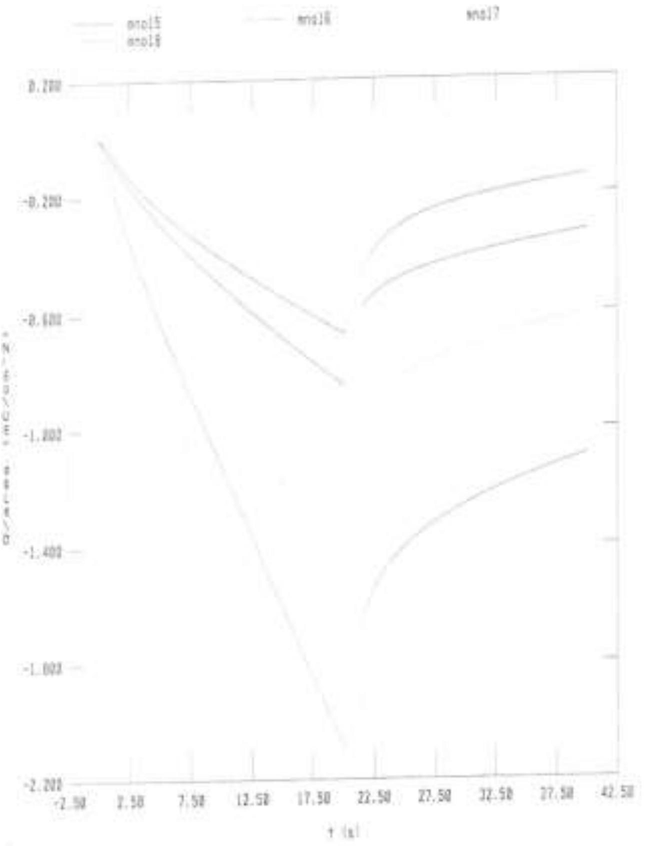


Figure 1.8: Chronocoulometry of T2

Table 1: X-ray diffraction data

Substrate temperature (^oC)	observed'd' values (Å)	standard'd' values (Å)	(hkl)	Phase	System
200 (T1)	1.1041	1.0945	(104)	$Mn(OH)_2$	Hexagonal
250 (T2)	4.7362	4.734	(001)	$Mn(OH)_2$	Hexagonal
	2.4169	2.42	(311)	λ-MnO_2	Cubic
300 (T3)	1.9321	2.0100	(400)	λ-MnO_2	Cubic

Table 2: Various electrochemical parameters deducted from Cyclic Voltammetry:

Sample	Scan rate mVS^{-1}	Ep_a 'mV'	Ep_c 'mV'	Ip_a 'μA/cm^{2}'	Ip_c 'μA/cm^{2}'	Δ Ep 'mV'	Area under the curve mC/cm^2	Contrast ratio	Diffusion coefficient $cm^2/sec\ 10^{-9}$	Insertion coefficient X
T2	10	560	360	8	60	200	8.946	1.35	0.62	0.0059
	20	525	530	12	66	5	4.504	1.35	1.48	0.0037
	50	560	510	21	70	50	1.968	1.35	3.50	0.0023
	100	575	595	23	72	20	0.995	1.35	7.22	0.0012
T1	10	370	300	240	50	70	20.71	--	0.08	--
	75	380	420	200	160	40	4.041	--	2.89	--
	100	400	560	160	200	160	3.355	--	4.93	--

Table 3: Various electrochemical parameters deducted from Chronoamperometry

Sample	Potential Step 'V'	T_c 'sec'	T_b 'sec'	Colouration Efficiency cm^2/C	Reversibility Q_{di}/Q_i	Q_i mC/cm^2	Δ OD mC/cm^2
250^0C(T2)	±1.0	12.52	32.07	17	0.528	2.12	12
	±0.8	11.89	30.36	12	0.455	1.32	12
	±0.6	11.66	32.88	9	0.475	0.80	12
	±0.4	10.69	31.85	6	0.307	0.65	12